

*Chiral H-bonded chains: a key to non-centrosymmetric co-crystals of 3,5-dinitropyridine-2(1H)-one*Ivan Fedyanin¹, Konstantin Lyssenko¹¹X-Ray Structural Centre, Institute Of Organoelement Compounds RAS, Moscow, Russian Federation

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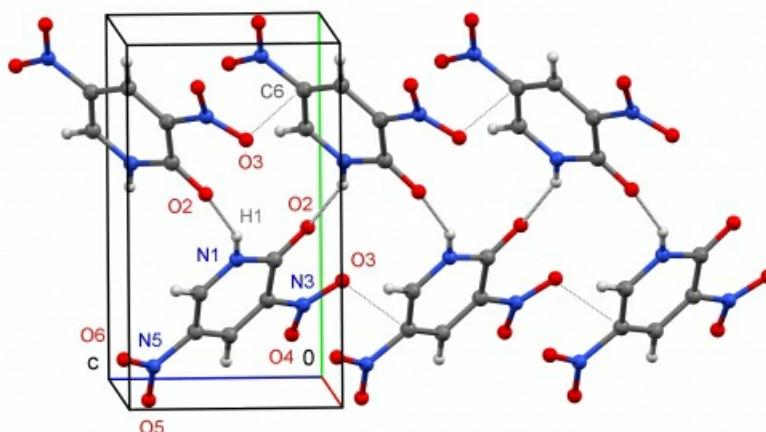
It is well known that organic molecules without chiral center tend to crystallize in centrosymmetric space groups, as this type of packing minimizes the interacting energy of bond dipoles. Although a chiral motif can be found in any structure with a screw axis, it does not usually influence the total crystal centrosymmetry.

In this work, we report crystal structures of two polymorphic forms of achiral 3,5-dinitropyridine-2(1H)-one (3,5DNP2O, sp. gr. Pna21 and P21), nine co-crystals with polyaromatic hydrocarbons (PAH) of different size, from naphthalene to perylene and a co-crystal with mono nitrosubstituted analogue (5NP2O), isostructural to monoclinic polymorph of 3,5DNP2O. The PAH molecules were used as "neutral" co-formers that do not disturb the H-bonding pattern and easily form multicomponent structures with electron-acceptor molecules. Of all structures, only three co-crystals are centrosymmetric. Instead of a very common synthon for cyclic amides, a centrosymmetric dimer, chiral hydrogen-bonded chains are found in all structures. The mutual orientation of 3,5DNP2O molecules in the chains is different in the polymorphs and the co-crystals, but some common features may be drawn. The chains are characterized by lower translation parameter (bc) in polymorphs, but significantly flattened and similarly rotated relative to 21 axis in co-crystals. The second type of supramolecular synthon in all co-crystals with PAH are infinite stacks of alternating 3,5DNP2O and PAH molecules connected by $n\dots n$ contacts.

All intermolecular interactions in crystals were thoroughly analyzed with a number of experimental and computational techniques, including high-resolution X-ray diffraction studies and ab initio calculations of crystals and isolated molecular associates. Two main conformations of the H-bonded chain can be distinguished, corresponding to the first and the second polymorph of 3,5DNP2O. Both conformations are relatively flexible, and stretching of the chains taken from the polymorphs lead to geometries found in co-crystals and vice versa. According to ab initio calculations, for certain values of translation parameter (bc) the second conformation is energetically more favorable than the first, and the value of bc for the monoclinic 3,5DNP2O polymorph falls exactly in this range. Based on experimental and theoretical data, we propose a possible mechanism for crystallization of less thermodynamically stable monoclinic polymorph, that can be only obtained in the presence of a specific aromatic admixture. The combination of chiral chains and n -stacks into 2D layers is considered to be the main reason for crystallization of co-crystals in space groups without inversion center.

The effectiveness in second harmonic generation (SHG) was evaluated experimentally and computed with periodic DFT methods for all non-centrosymmetric structures. The orthorhombic polymorph of 3,5DNP2O demonstrates high SHG efficiency (1.4 times higher than for N-(4-nitrophenyl)-(L)-prolinol reference). Co-crystallization with PAH lowers the efficiency, but it remains relatively high for specific arrangement of molecules, in co-crystals with naphthalene and phenanthrene.

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